

[REDACTED]

[REDACTED]

Subject **Leaching of peroxide degradation products from a gelcoat cured with [REDACTED]**

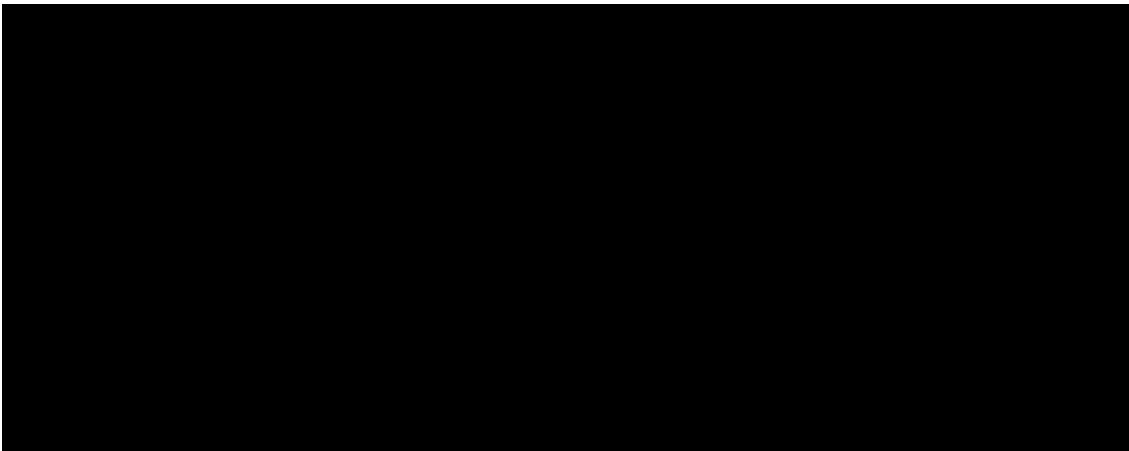
CONFIDENTIAL

Summary

A headspace gas chromatography method for the determination of [redacted] in aqueous extracts from a gelcoat was successfully developed. The target compounds are adequately resolved from impurity peaks. The method yields linear calibration lines, offers a good precision and offers sub-ppm detection (LOD) and quantitation (LOQ) limits:

	Precision		Precision		LOD, mg/l	LOQ, mg/l
	conc., mg/l	sd., %	conc., mg/l	sd., %		
Ultrapure water	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]

A leaching study was conducted at 40°C. A gelcoat manufactured with use of [redacted] was contacted during 10 days with ultrapure water or with seawater simulant, the area-to-volume ratio being 6 dm²/l. In the ultrapure water samples, 4.9 mg/l Isopropyl acetate and 21.8 mg/l [redacted] were measured. In the seawater simulant samples 4.2 mg/l Isopropyl acetate and 18.8 mg/l [redacted] were found. [redacted] was detected in all samples; its concentration remained below the quantitation limit.



1. Introduction

██████████ is a high reactive ██████████ which is particularly suitable for the curing of gelcoat resins and laminating resins used for the production of boat hulls and deck parts. During the curing process, peroxide decomposition products are formed which may be transferred when the gelcoat is brought in contact with (sea)water. This may cause damage to the marine environment. At the request of the Belgian authorities, a leaching study was conducted to investigate this aspect.

2. Experimental section

2.1 Samples, standards and chemicals

Samples

Six glass fiber reinforced polyester sheets, length 27 cm, 11 cm wide, thickness 2.5 mm; each bearing on one side a gelcoat with a thickness of 0.45 mm.

██████████ (approx. 2 mass%) was used for the curing of both the polyester and the gelcoat.

Standards

Isopropylacetate	: CAS 108-21-4, 99% pure, Acros Organics, Geel, Belgium
3-Methyl-2-butanone	: CAS 563-80-4, 98% pure, Acros Organics, Geel, Belgium
3-Methyl-2-butanol	: CAS 598-75-4, 98% pure, Acros Organics, Geel, Belgium

Chemicals

Acetone	: Analyzed grade, J.T. Baker, Deventer, The Netherlands.
Water	: Ultrapure : resistivity > 10 MΩ·cm, TOC < 10 ppb, purified with a Milli-Q apparatus, Millipore, Billerica (MA), USA.
Sodium Chloride	: Analytical grade, J.T. Baker, Deventer, The Netherlands.
Seawater simulant	: 30 grams Sodium chloride are dissolved in 1 liter ultrapure water

2.2 Instrumentation

Standard equipment

- Analytical balance	: Mettler AE163, readable to 0.01 mg
- Bulb pipettes	: 'Blau' grade, Brand, Germany
- Positive displacement pipettes	: Microman, Gilson, France
- Volumetric flasks	: 'Blau' grade, Brand, Germany
- graduated 5µl GC syringe	: Hamilton, Switzerland.
- 20 ml septum vials	: with Teflon lined septum and aluminum crimp cap. Thermo Fisher Scientific, The Netherlands.

GC-MS

Finnegan SSQ 7000 mass spectrometer coupled to an Agilent 6890 gas chromatograph.

Headspace-GC

- Agilent 5890 series II plus gas chromatograph provided with a Triplus autosampler (Interscience, Breda, The Netherlands.)
- Chromatography data system : Atlas, version 7.10.9, Thermo Instruments, The Netherlands

2.3 Procedures

GC conditions

Column	: fused silica, 25 m x 0.32 mm ID, Varian, The Netherlands
- stationary phase	: WAX for amines
- film thickness	: 1.2 μ m
Carrier gas	: helium
- flow	: methane time : 62 \pm 2 sec (at 40°C)
Injector	: split
- split flow	: 60 ml/min.
- glass insert	: containing a plug of silanized glass wool
Temperatures	
- split injector	: 150°C
- detector	: 310°C
- column	: initial : 40°C during 2 min rate A : 4°C/min final A : 80°C rate B : 20°C/min final B : 225°C during 5 min

Headspace sampler conditions

Oven temperature	: 80°C
Equilibration time	: 30 minutes
Injection volume	: 1 ml

Calibration lines

Two stock solutions were prepared:

A: 744 mg 3-methyl-2-butanone, 241 mg Isopropylacetate and 240 mg 3-methyl-2-butanol were dissolved in 10 ml Acetone.

B: 526 mg 3-methyl-2-butanone, 175 mg Isopropylacetate and 140 mg 3-methyl-2-butanol were dissolved in 10 ml Acetone.

Four additional solutions were prepared by diluting aliquots of A and B respectively 2x and 20x with Acetone.

Two groups of 20 ml septum vials were filled with 10 ml of either ultrapure water or seawater simulant. To each vial, 4.0 μ l of one of the above solutions was added using a calibrated GC syringe. The vials were then sealed and analyzed.

Leaching test

Rectangular test strips with dimensions of 10 (± 0.5) mm x 30 (± 0.5) mm were cut out of the polyester sheets - thereby avoiding to take a sample at the very edges of the sheet.

A group of septum vials were each loaded with two strips which were positioned back-to-back, to prevent the migration of compounds from the backside of the strips. To each vial, 10 ml of ultrapure water or 10 ml of seawater simulant was added.

Using crimp caps, the vials were sealed with a Teflon-lined septum and were placed in a GC oven which was kept at 40°C.

After 10 days, the vials were transferred to the headspace sampler and were analyzed.

3. Results and discussion

The [REDACTED] forming the active ingredients from [REDACTED] are predicted to be degraded completely during the curing process, especially since the added catalyst is not consumed. The compounds generated in the decomposition process may be partially retained by the gelcoat and may be transferred when the gelcoat is brought in contact with water. A leaching study was performed to investigate this aspect.

3.1 Method development and validation.

Resolution and specificity

The major decomposition products expected to be formed are Carbon dioxide, Propane, Acetic Acid, Acetone, Isopropyl acetate, [REDACTED] and [REDACTED]. These compounds are all volatiles, so it was decided to use headspace gas chromatography for their analysis.

A pilot study was conducted using a non-polar column and GC-MS detection. Water extracts from a polyester test strip appeared to contain several volatile compounds, at a level of around 10 mg/l (ppm). Propane, Propene, Acetone, Isopropyl acetate, 3-Methyl-2-butanone and possibly 3-Methyl-2-butanol were identified in the first part of the chromatogram, together with Benzene, which is a known byproduct present in polyester. At higher retention times several aromatic impurities, e.g. Styrene, were found, but additional decomposition products from the peroxide were not detected amongst these peaks.

On the non-polar column, Benzene partially coelutes with Isopropylacetate and with 3-Methyl-2-butanol. This could not be remedied by adapting the oven temperature program, so alternative stationary phases were investigated. Carbowax appeared to provide the best resolution.

The final conditions for the developed headspace-GC method are listed in paragraph 2.3.

A chromatogram recorded from a test sample prepared from pure standards is shown in appendix 1. Benzene, Isopropylacetate and 3-Methyl-2-butanone are seen to be baseline separated, be it just. 3-Methyl-2-butanol is fully resolved from any neighboring peaks.

The chromatogram illustrates that compounds with a similar concentration may yield peaks with very different areas, indicating that these compounds have rather different water/air partition coefficients and will consequently have differing detection limits.

Linearity and precision

Standard solutions containing Isopropyl acetate, [REDACTED] [REDACTED] were prepared in ultrapure water and in seawater simulant. The solutions covered a concentration range from 1 to 30 mg/l.

The peak areas measured from these solutions are listed in appendix 2, the calibration lines constructed from these data are also illustrated.

All calibration lines appear to be linear and to have acceptable regression coefficients. The slopes of the lines measured from the solutions in seawater simulant are significantly larger (approximately 20%) than the slope of the lines measured from solutions in ultrapure water. Apparently, the addition of Sodium chloride promotes the migration of the compounds into the gas phase. This behavior is well documented and is commonly known as the 'salting out' effect.

The precision of the method was determined from repeated injections of the test solution illustrated in appendix 1. The relative standard deviations were found to be 0.91% for Isopropylacetate, 0.94% for [REDACTED] and 2.1% for [REDACTED]. Precision data were also calculated from repeat determinations made during the measurement of the calibration lines. See appendix 2B. This time, four identical dilutions from the same stock solution were prepared and were individually analyzed. For the dilutions made in ultrapure water, relative standard deviations were calculated of: 3.4% for 3.5 mg/l Isopropyl acetate, 3.3% for 10.5 mg/l 3-Methyl-2-butanone and 3.8% for 2.8 mg/l 3-Methyl-2-butanol. For the dilutions made in seawater simulant, the corresponding relative standard deviations were respectively 3.0%, 3.2% and 1.5%.

Detection limit (LOD), Quantitation limit (LOQ)

Typical chromatograms from standard solutions containing approximately 3 mg/l of 3-Methyl-2-butanone and 1 mg/l of Isopropylacetate and of 3-Methyl-2-butanol are illustrated in appendix 3. From these chromatograms, the detection and quantitation limits of the method were determined according to a procedure taken from the European Pharmacopoeia (ref.5.1).

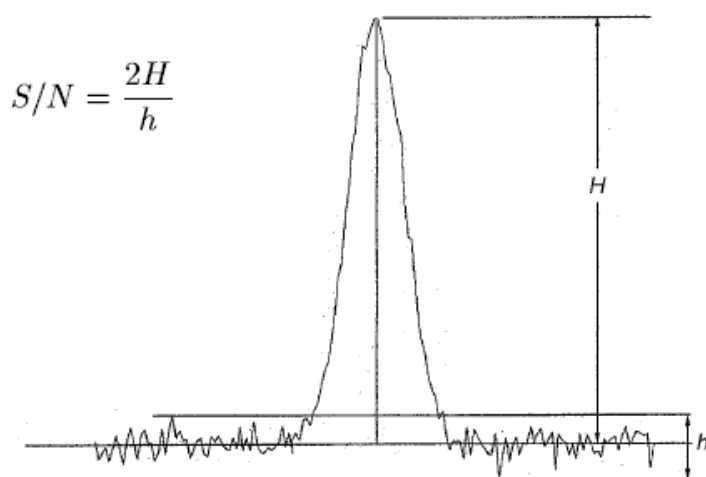


Figure 1. Determination of the S/N ratio.

The height of a peak and the height of the baseline noise are measured and the signal-to-noise ratio (S/N) is determined as illustrated in figure 1.

The LOD and LOQ values are defined as:

LOD : concentration corresponding to a S/N ratio of 3.

LOQ : concentration corresponding to a S/N ratio of 10.

From the standard solution in ultrapure water, LOD/LOQ values of 0.029/0.096 mg/l, 0.046/0.15 mg/l and 0.089/0.30 mg/l were measured for respectively Isopropylacetate, 3-Methyl-2-butanone and 3-Methyl-2-butanol.

From the standard solution in seawater simulant, LOD/LOQ values of 0.029/0.096 mg/l, 0.047/0.16 mg/l and 0.095/0.32 mg/l were measured for respectively Isopropylacetate, 3-Methyl-2-butanone and 3-Methyl-2-butanol.

Leaching test

After having developed the method, a leaching test was conducted.

Polyester test strips covered with a gelcoat were contacted with ultrapure water or with seawater simulant during 10 days at a temperature of 40°C, the applied area-to-volume ratio being 6 dm²/l. The results are listed in appendix 4.

A typical chromatogram from the contact liquid is illustrated (4B), which shows the peroxide degradation products Propane, Propene, Acetone, Isopropylacetate, 3-Methyl-2-butanone and 3-Methyl-2-butanol. In addition, typical impurities from polyester are detected, like Benzene and Styrene. These compounds must have migrated from the sides of the test strips, which are not covered with the gelcoat.

In the ultrapure water contact samples, 4.9 mg/l Isopropyl acetate and 21.8 mg/l 3-Methyl-2-butanone were measured, the relative standard deviation being 5.4%.

In the seawater simulant contact samples 4.2 mg/l Isopropyl acetate and 18.8 mg/l 3-Methyl-2-butanone were measured, the relative standard deviation being 4.4%.

3-Methyl-2-butanol was detected in all samples; its concentration remained below the quantitation limit.

- A headspace gas chromatography method for the determination of Isopropyl acetate, [REDACTED] in aqueous extracts from a gelcoat was successfully developed.

[illegible]

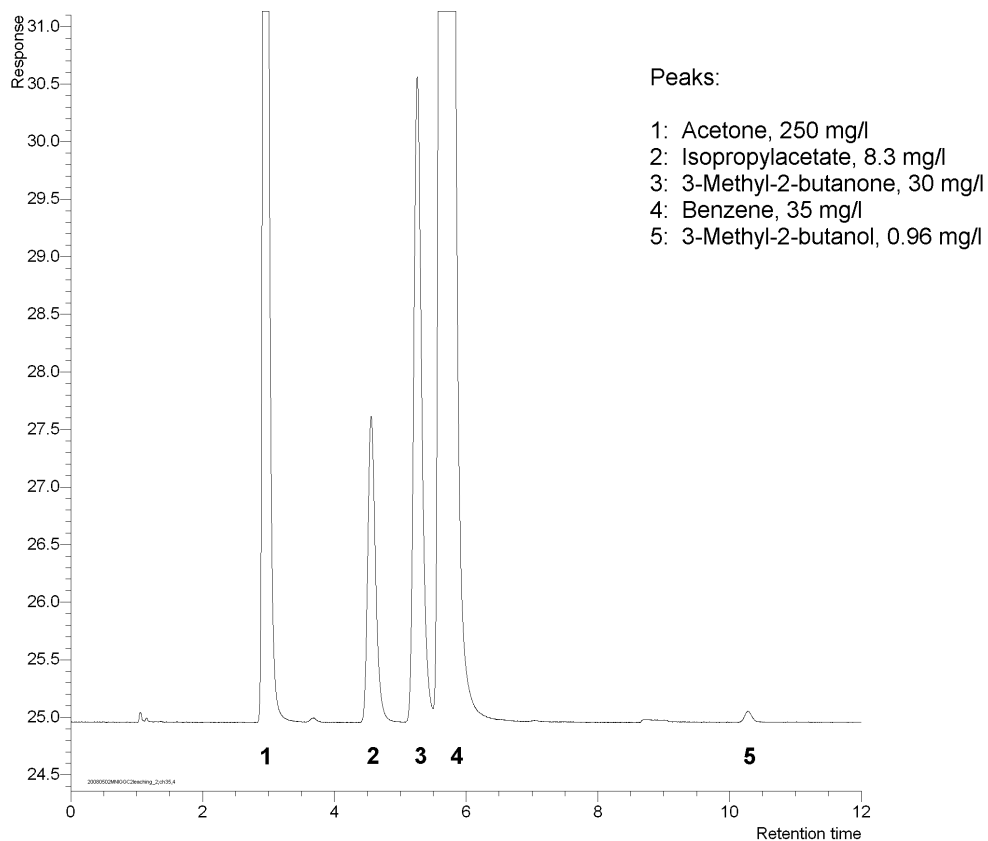
- Using GC-MS, the peroxide degradation products Propane, Propene, Acetone, Isopropyl acetate, [REDACTED] were identified in leachates from the gelcoat.
- A leaching study was conducted at 40°C. A gelcoat manufactured with use of [REDACTED] peroxide was contacted during 10 days with ultrapure water or with seawater simulant, the area-to-volume ratio being 6 dm²/l. In the ultrapure water samples, 4.9 mg/l Isopropyl acetate and 21.8 mg/l [REDACTED] were measured, the relative standard deviation being 5.4%. In the seawater simulant samples 4.2 mg/l Isopropyl acetate and 18.8 mg/l [REDACTED] were measured, the relative standard deviation being 4.4%. [REDACTED] was detected in all samples; its concentration remained below the quantitation limit.

7. Appendices

- Appendix 1. Gas chromatogram of a test sample prepared in seawater simulant and precision data calculated from 5-fold injections of this test sample.
- Appendix 2. Calibration lines, precision data and gas chromatograms obtained from standard solutions prepared in ultrapure water or in seawater simulant.
- Appendix 3. Chromatograms from standard solutions containing 3 mg/l [REDACTED] 1 mg/l Isopropylacetate, and 1 mg/l [REDACTED]. Detection limits and quantitation limits of the GC method.
- Appendix 4. Peak area data and typical chromatograms measured for Isopropylacetate, [REDACTED] from samples of ultrapure water and seawater simulant which have been contacted at 40°C during 10 days with test strips covered with a gelcoat.

Appendix 1. 1A: Gas chromatogram of a test sample prepared in seawater simulant.
1B: Precision data calculated from 5-fold injections of this test sample.

1A.



1B.

Vial nr.	Area, $\mu\text{V}\cdot\text{sec}$		
	Isopropylacetate	3-Methyl-2-butanone	3-Methyl-2-butanol
1 *	* 21797	* 47047	* 742
2	26579	57866	881
3	26413	57246	902
4	26926	58583	857
5	26866	57872	872
Average	26696	57892	878
sd.	242	546	18.8
sd., %	0.91	0.94	2.1

* outlier: excluded from sd. calculation

Appendix 2. Calibration lines, precision data and gas chromatograms obtained from standard solutions prepared in ultrapure water or in seawater simulant.

2A. Peak areas measured from calibration solutions

Ultrapure water

Isopropylacetate		[REDACTED]		[REDACTED]	
mg/l	Area	mg/l	Area	mg/l	Area
0.35	1058	1.05	1942	0.28	255
0.96	2867	2.97	5521	0.96	797
3.50	9341	10.53	17334	2.79	2179
4.81	12261	14.87	23757	4.80	3656
7.01	18844	21.06	35140	5.58	4363
9.62	24662	29.75	47417	9.61	7329

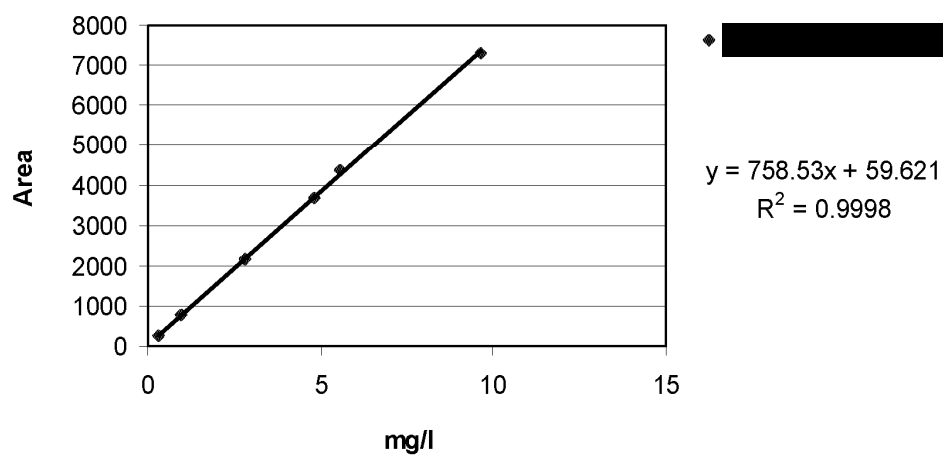
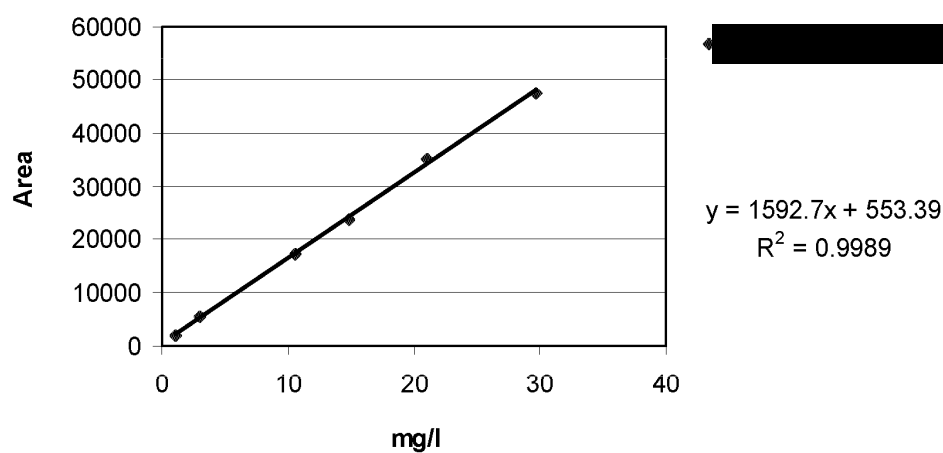
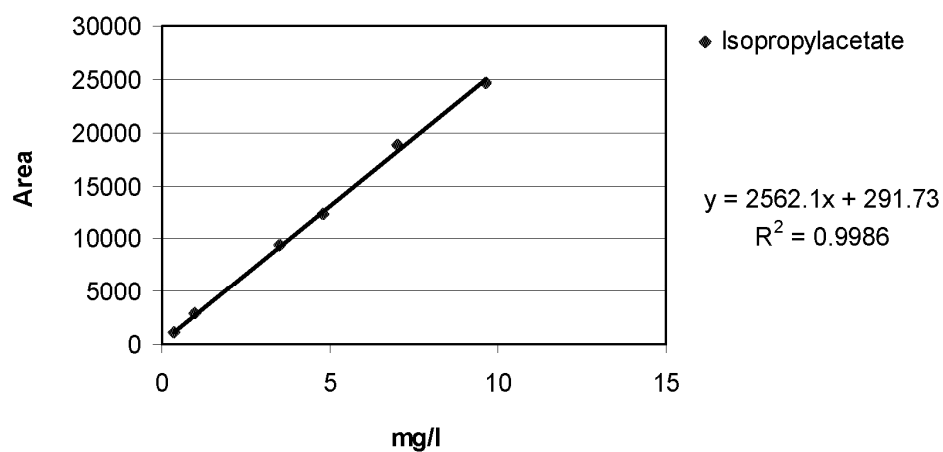
Seawater simulant

Isopropylacetate		[REDACTED]		[REDACTED]	
mg/l	Area	mg/l	Area	mg/l	Area
0.35	1347	1.05	2424	0.28	319
0.96	3234	2.97	6102	0.96	925
3.50	11427	10.53	21046	2.79	2735
4.81	15643	14.87	29547	4.80	4563
7.01	22403	21.06	41303	5.58	5319
9.62	30725	29.75	58330	9.61	9364

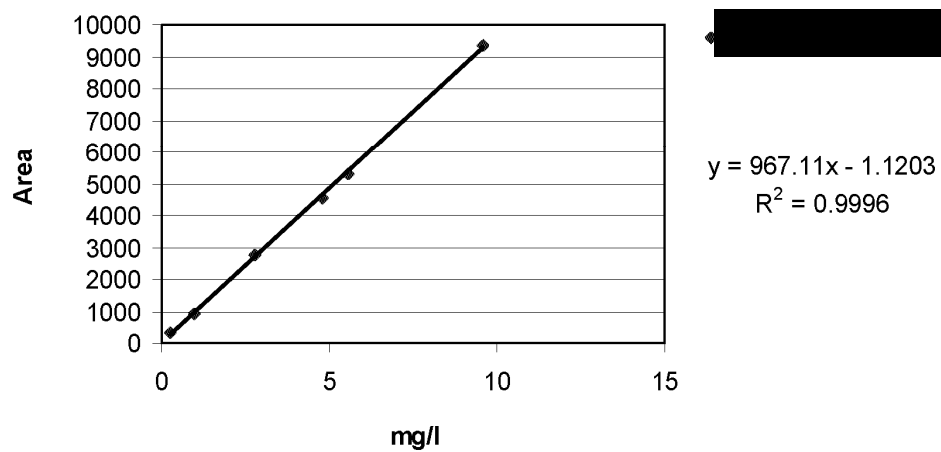
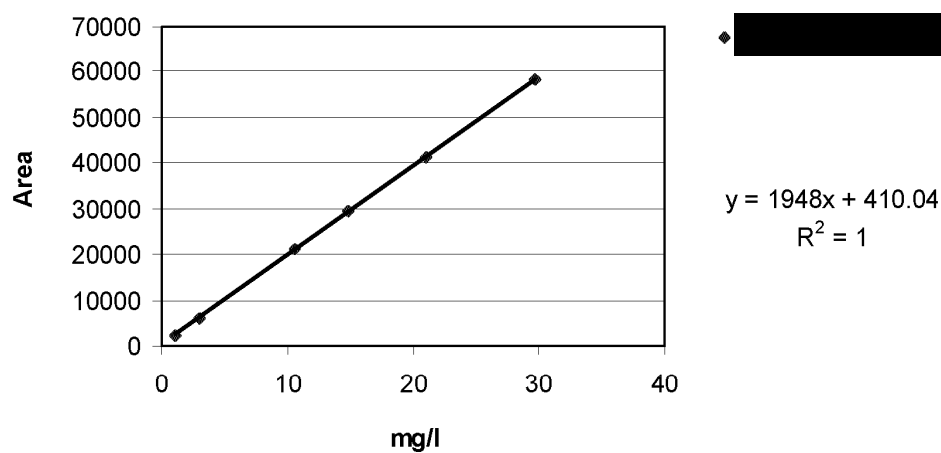
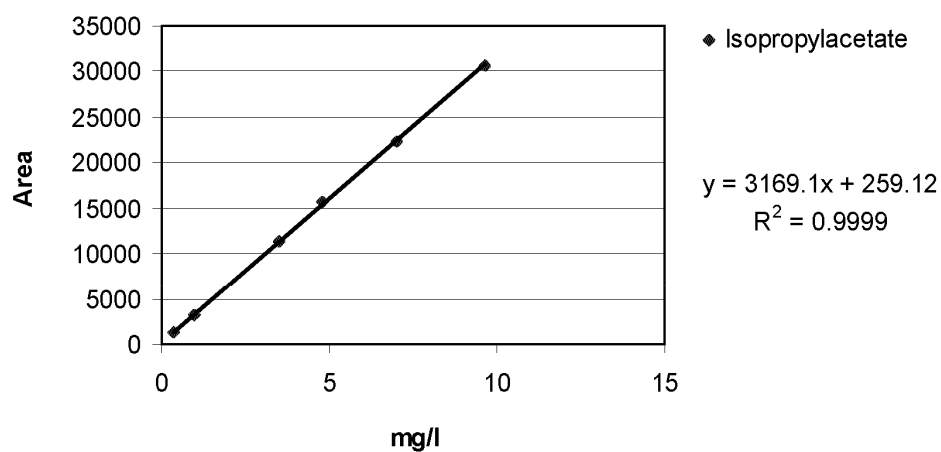
2B. Peak area data and their standard deviations measured from multiple determinations on two standard solutions prepared with ultrapure water and with seawater simulant.

Ultrapure water, vial nr.	Isopropylacetate 3.5 mg/l	Area, $\mu\text{V}\cdot\text{sec}$	
		10.5 mg/l	2.8 mg/l
1	9341	17334	2179
2	8911	16616	2028
3	9309	17309	2080
4	9684	17999	2195
Average	9311	17315	2121
s.d.	316	565	80
s.d., %	3.4	3.3	3.8
Seawater simulant, vial nr.			
5	11427	21046	2735
6	11631	21415	2690
7	12204	22601	2775
8	12005	22140	2690
Average	11817	21800	2723
s.d.	352	701	41
s.d., %	3.0	3.2	1.5

2C. Calibration lines obtained from the standard solutions prepared with Ultrapure water.

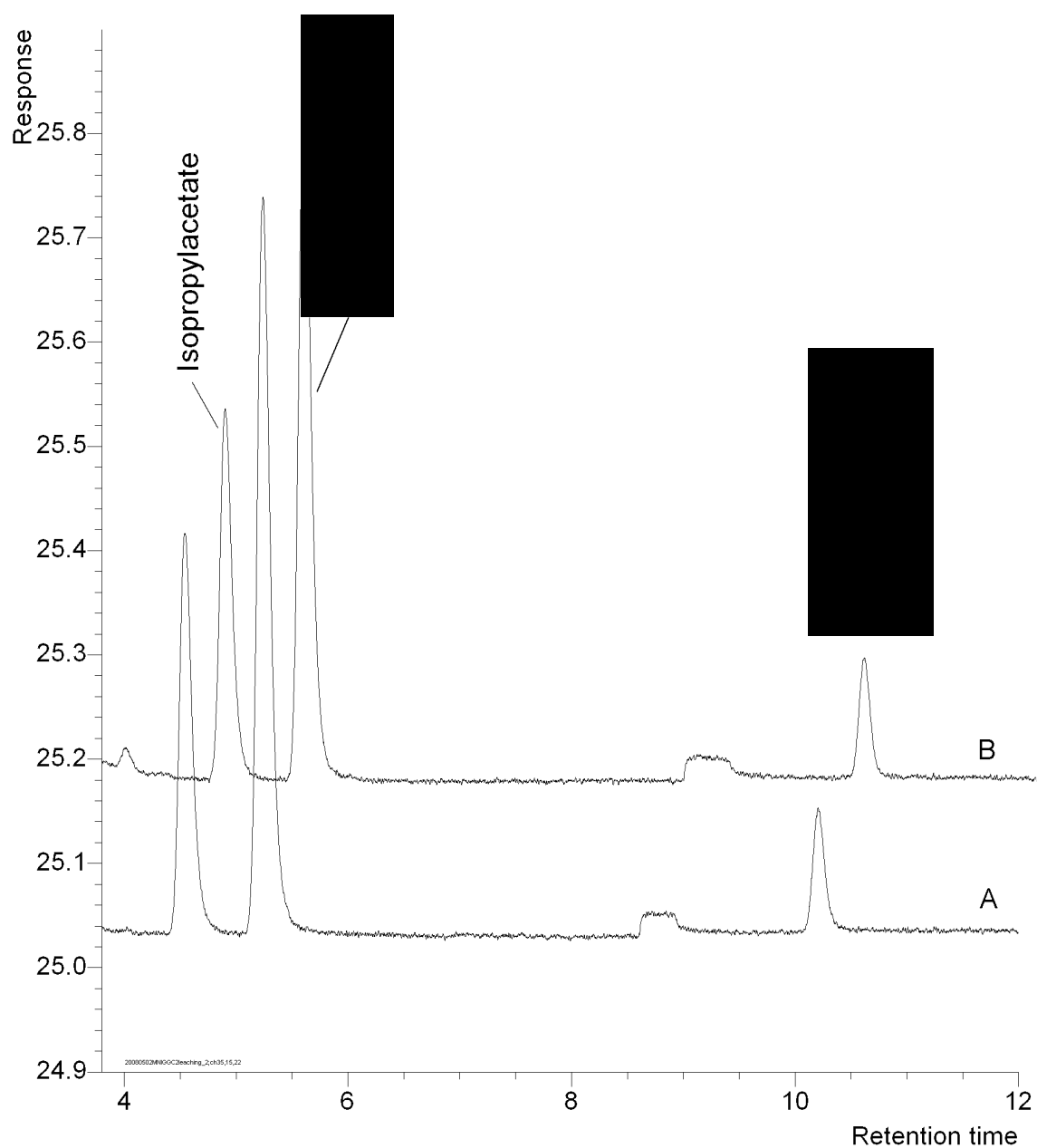


2D. Calibration lines obtained from the standard solutions prepared with seawater simulant.



Appendix 3. Chromatograms from standard solutions containing 3 mg/l [REDACTED] 1 mg/l Isopropylacetate, and 1 mg/l [REDACTED]. From these chromatograms, the detection limits and quantitation limits of the GC method were determined.

3A. Chromatograms from solutions prepared in seawater simulant (A) or in ultrapure water (B).





AkzoNobel
Tomorrow's Answers Today

3B. Calculated detection limits (LOD) and quantitation limits (LOQ).

Ultrapure water	Isopropylacetate		
LOD, mg/l	0.029	0.046	0.089
LOQ, mg/l	0.096	0.15	0.30
Seawater simulant	Isopropylacetate	3-Methyl-2-butanone	3-Methyl-2-butanol
LOD, mg/l	0.029	0.047	0.095
LOQ, mg/l	0.096	0.16	0.32

Appendix 4. Peak area data and typical chromatograms measured for Isopropylacetate and [REDACTED] from samples of ultrapure water and seawater simulant which have been contacted at 40°C during 10 days with test strips covered with a gelcoat. [REDACTED] as also detected but its concentration remained below the quantitation limit.

4A.

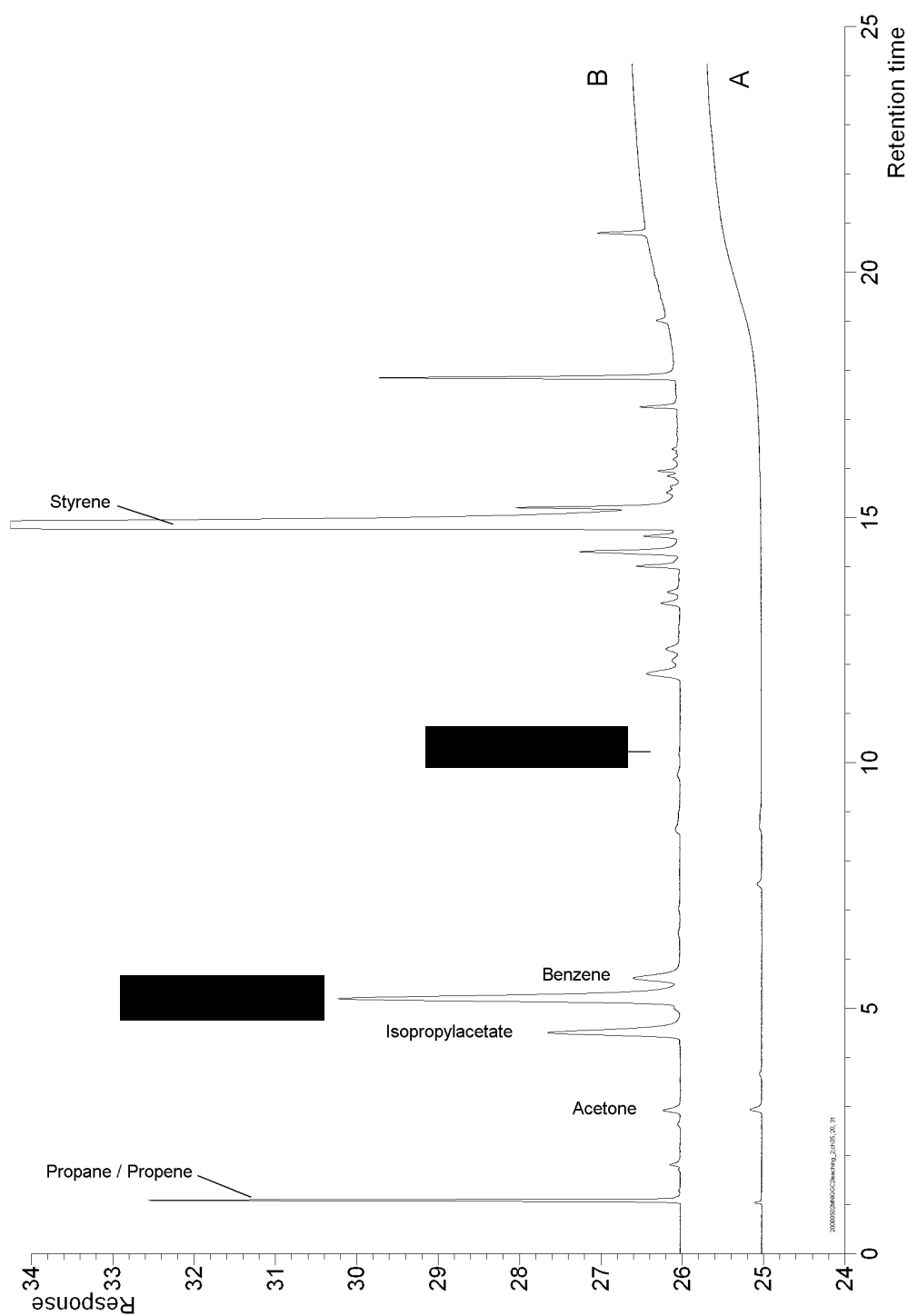
Ultrapure water

Test strip nr.	Area, $\mu\text{V}\cdot\text{sec}$	
	Isopropylacetate	[REDACTED]
1	13846	38221
2	13421	36710
3	12361	34231
4	12061	33090
5	12381	33946
Average	12814	35240
s.d.	692	1916
s.d., %	5.4	5.4
Concentration, mg/l	4.89	21.8

Seawater simulant

Test strip nr.	Area, $\mu\text{V}\cdot\text{sec}$	
	Isopropylacetate	[REDACTED]
6	13993	37600
7	14430	38982
8	13722	37800
9	12812	34278
10	12992	36304
Average	13590	36993
s.d.	608	1601
s.d., %	4.5	4.3
Concentration, mg/l	4.21	18.8

- 4B. Typical gas chromatograms of fresh seawater simulant (A) and of a seawater simulant sample contacted at 40°C during 10 days with the gelcoat (B). Chromatograms from ultrapure water contact samples were very similar to the seawater simulant chromatogram.



- 4C.** Expanded view of the [REDACTED] region from gas chromatograms of:
- a: blank: ultrapure water
 - b: blank: seawater simulant
 - c: seawater simulant sample contacted at 40°C during 10 days with the gelcoat
 - d: ultrapure water sample contacted at 40°C during 10 days with the gelcoat
 - e: standard solution, containing 1.05 mg/l [REDACTED]

